spectra observed in octahedral symmetry are dominated by the vibronic transitions. Furthermore, the electrostatic, spin–orbit, and crystalline field parameters increase as the ligand changes from I^- to F^-. In the $5f^1$ series the crystalline field and spin–orbit parameters also increase with higher oxidation state on the metal ion. The reported analysis of the optical spectrum of $CsNpF_6$[24] does not fit the above trends. We suggest this discrepancy should be studied further.

Conclusion

We have analyzed the optical spectra of $(NEt_4)_2UF_6$ and $(NEt_4)_2UI_6$. The electrostatic, spin–orbit, and crystal field parameters for the entire UX_6^{2-} (X = F, Cl, Br, I) have been obtained and where applicable compared to corresponding parameters for PaX_6^{2-}. It was noted that the Slater parameter F^2 changes by approximately 20% for the series and the crystal field parameters are dissimilar for the comparable PaX_6^{2-} and UX_6^{2-} complexes.

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Registry No. $(Et_4N)_2UF_6$, 42294-80-4; $(Et_4N)_2UI_6$, 56848-06-7; Cs_2UCl_6, 17030-13-6; $(NEt_4)_2UCl_6$, 12081-51-5; $(NEt_4)_2UBr_6$, 12080-72-7.

References and Notes

(1) (a) Lawrence Berkeley Laboratory. (b) Atomic Energy Research Establishment.
(2) (a) N. Edelstein, D. Brown, and B. Whittaker, *Inorg. Chem.*, **13**, 563 (1974); (b) D. Brown, B. Whittaker, and N. Edelstein, *ibid.*, **13**, 1805 (1974).
(3) D. Brown, P. Lidster, B. Whittaker, and N. Edelstein, *Inorg. Chem.*, **15**, 214 (1976).
(4) D. R. Johnston, R. A. Satten, C. L. Schreiber, and E. Y. Wong, *J. Chem. Phys.*, **44**, 3141 (1966).
(5) R. A. Satten, C. L. Schreiber, and E. Y. Wong, *J. Chem. Phys.*, **42**, 162 (1965).
(6) R. A. Satten, D. Young, and D. M. Gruen, *J. Chem. Phys.*, **33**, 1140 (1960).
(7) D. Brown, B. Whittaker, and J. Edwards, Report AERE-R7480, Atomic Energy Research Establishment, 1973 (available from H. M. Stationary Office, London, W.C.1, England).
(8) B. R. Judd, "Operator Techniques in Atomic Spectroscopy", McGraw-Hill, New York, N.Y., 1963.
(9) B. G. Wybourne, "Spectroscopic Properties of Rare Earths", Interscience, New York, N.Y., 1965.
(10) In our calculations we have used as the electrostatic interaction parameters the Slater radial integrals F^k ($k = 2, 4, 6$). These integrals have been redefined by Condon and Shortley[11] as $F_2 = F^2/225$, $F_4 = F^4/1089$, and $F_6 = F^6/7361.64$, for an f^n configuration.
(11) E. U. Condon and G. H. Shortley, "The Theory of Atomic Spectra", Cambridge University Press, Cambridge, 1935.
(12) K. Rajnak, *Phys. Rev. A*, **14**, 1979 (1976).
(13) W. von der Ohe, *J. Chem. Phys.*, **62**, 3933 (1975).
(14) J. Shamir and A. Silberstein, *J. Inorg. Nucl. Chem.*, **37**, 1173 (1975).
(15) S. L. Chodos and R. A. Satten, *J. Chem. Phys.*, **62**, 2411 (1975).
(16) D. Brown, B. Whittaker, and P. E. Lidster, Report AERE-R8035, Atomic Energy Research Establishment, 1975 (available from H. M. Stationary Office, London, W.C.1, England).
(17) J. L. Ryan, J. M. Cleveland, and G. H. Bryan, *Inorg. Chem.*, **13**, 214 (1974).
(18) W. T. Carnall, private communication.
(19) B. R. Judd, private communication.
(20) B. R. Judd, *Math. Proc. Cambridge Philos. Soc.*, in press.
(21) C. E. Schäffer and C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **8**, 143 (1958).
(22) K. Rajnak and B. G. Wybourne, *J. Chem. Phys.*, **41**, 565 (1964).
(23) S. S. Bishton and D. J. Newman, *J. Phys. C*, **3**, 1753 (1970).
(24) L. P. Varga, J. D. Brown, M. J. Reisfeld, and R. D. Cowan, *J. Chem. Phys.*, **52**, 4233 (1970).

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Kinetics and Mechanism of the Oxidation of Arsenic(III) by Hexacyanoferrate(III) in Alkaline Medium

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Kinetics of the reaction between hexacyanoferrate(III) and arsenic(III) in alkaline medium has been reinvestigated to establish As^{III} and OH^- dependences. The rate depends on the ratio $[OH^-]/[As^{III}]$. The rate law for $[OH^-]/[As^{III}] > 1$ is $-d[Fe(CN)_6^{3-}]/dt = [Fe(CN)_6^{3-}][As^{III}](k_1K_1[OH^-] + k_2K_1K_2[OH^-]^2 + k_3K_1K_2K_3[OH^-]^3)/(1 + K_1[OH^-] + K_1K_2[OH^-]^2 + K_1K_2K_3[OH^-]^3)$. k_1, k_2, and k_3K_3 were found to be $(10 \pm 0.9) \times 10^{-3}$ M^{-1} s^{-1}, 0.35 ± 0.02 M^{-2} s^{-1}, and 13 ± 0.2 M^{-3} s^{-1}, respectively, at 45 °C and $I = 2.0$ M. K_1, K_2, and K_3 are the equilibrium constants for the formation of $H_2AsO_3^-$, $HAsO_3^{2-}$, and AsO_3^{3-} from H_3AsO_3 and OH^-. E_a and ΔS^* associated with k_1, k_2, and k_3K_3 were found to be 11.8 ± 0.5, 6.4 ± 0.7, and 3.75 ± 0.46 kcal mol^{-1} and -32 ± 2, -43 ± 3, and -42 ± 3 cal mol^{-1} deg^{-1}, respectively.

Introduction

Krishna and Singh[1] and Mushran and co-workers[2] have investigated the kinetics of the oxidation of arsenic(III) by hexacyanoferrate(III) ion in alkaline solutions. The effect of hexacyanoferrate(III) ion has been variously reported. A limited range of concentrations had been employed to study the arsenite and hydroxide ion dependences. The various equilibria involving arsenic(III) and OH^-, as reported by Mushran and co-workers,[2] clearly indicate that the arsenite and hydroxide ion dependences would depend on their ratios but they did not give quantitative treatment. These were some of the points which prompted us to reinvestigate the kinetics of this reaction. About a 1000-fold variation in the concentration of As^{III} and about 500-fold variation in the concentration of NaOH have enabled us to characterize the various rate constants. The overall reaction is represented by

$$As^{III} + 2Fe(CN)_6^{3-} \rightarrow As^V + 2Fe(CN)_6^{4-}$$

Experimental Section

The stock solution of 0.2 N arsenious acid was prepared by dissolving the requisite amount of arsenic trioxide, sufficient to give a little more than 0.20 N acid, in boiling water. After cooling, it was filtered and standardized against a standard permanganate solution. All other reagents used were BDH AnalaR. Doubly distilled water was used throughout (the second distillation being from the permanganate).

Reactions were carried out in a thermostated water bath at 45 ± 0.1 °C unless mentioned otherwise. Measured quantities of As^{III} and sodium hydroxide solutions were mixed and kept in the water bath

Table I. Effect of $Fe(CN)_6^{3-}$ on the Rate of the Reaction between $Fe(CN)_6^{3-}$ and As^{III} [a]

$10^4[Fe(CN)_6^{3-}]$, M	10^6(rate of decrease of $[Fe(CN)_6^{3-}]$), M s^{-1}	$10^4[Fe(CN)_6^{3-}]$, M	10^6(rate of decrease of $[Fe(CN)_6^{3-}]$), M s^{-1}
2.00	0.51	8.00	2.27
3.00	0.75	9.00	2.47
4.00	1.10	10.0	3.04
5.00	1.43	12.0	3.42
6.00	1.78	14.0	3.91
7.00	2.17	15.0	3.96

[a] $[As^{III}] = 1.0 \times 10^{-2}$ M; $[NaOH] = 5.0 \times 10^{-2}$ M; $I = 1.0$ M (made up by NaCl); 45 °C; wavelength 420 nm.

to attain its temperature. The reaction was started by mixing temperature-equilibrated potassium hexacyanoferrate(III) solution. The progress of the reaction was followed by measuring[3] the absorption of hexacyanoferrate(III) at 415 nm on a Spectronic 20 colorimeter. The hexacyanoferrate(II)[4] is almost transparent at this wavelength.

Reactions of hexacyanoferrate(III) in general are strongly influenced by salts. The rate increases because of the ion-pair formation[5] and/or a positive salt effect[6] as found in the oxidations of sulfite,[7] selenium(IV),[8] and ascorbic acid.[9] Hence most of the reactions were carried out in the presence of excess sodium chloride so that the above effects as a result of the reaction could be minimized. There was no effect of chloride on the reaction rate. No spectrophotometric or kinetic evidence for As^{III}–Cl^- complexes was obtained.

pH measurements were made on Expand pH meter 821 of Electronics Corp. and hydroxyl ion concentrations were calculated from these observations. Spectrophotometric measurements were made on a Beckman DU-2 spectrophotometer.

Pseudo-first-order rate constants were calculated from a plot of log $[Fe(CN)_6^{3-}]$ vs. time when arsenite was in large excess and the second-order rate constants were derived from this. In other cases second-order rate constants were calculated from a plot of log $([As^{III}]/[Fe(CN)_6^{3-}])$ vs. time. In case of arsenite variation, initial rates were calculated by the plane mirror method.[10]

Duplicate measurements were reproducible to ±5%.

Results

Hexacyanoferrate(III) Dependence. The concentration was varied in the range $(2–15) \times 10^{-4}$ M and the results are given in Table I. A log–log plot of rate and concentration yielded a straight line with a slope of 1.05 ± 0.05. The order in hexacyanoferrate(III) is thus 1 and does not vary in the concentration range studied. Mushran and co-workers[2] have also reported an order of one whereas Krishna and Singh[1] found the order to vary slightly.

Arsenite Dependence. The concentration of arsenite was varied from 2×10^{-4} to 1.6×10^{-1} M at three different concentrations of sodium hydroxide and a fixed concentration of hexacyanoferrate(III). The first-order dependence on arsenite is obvious when the ratio $[OH^-]_T/[As^{III}]$ is large. The previous workers made an investigation in this range and found the order in arsenite to be 1. A maximum in the rate is found when the ratio $[OH^-]_T/[As^{III}] \simeq 4$. The rate appears to attain a limiting value when this ratio is less than 1. For the three concentrations of sodium hydroxide, the limiting rate is almost in proportion to the concentration of the hydroxide. The values of the initial rates divided by the hydroxide ion and hexacyanoferrate(III) concentrations are 10.4×10^{-3}, 9.8×10^{-3}, and 9.8×10^{-3} M^{-1} s^{-1} for 0.1, 0.05, and 0.025 M NaOH, respectively. Although the arsenite dependence appears to be complex, it is simple first order as shown later, but it cannot be shown experimentally owing to the variation in the ratio $[OH^-]_T/[As^{III}]$. The rate depends on the concentration of the species formed from As^{III} and OH^-. The formation constant for the species $H_2AsO_3^-$ is large, and hence under excess arsenite condition, the rate depends on the hydroxide concentration and appears to be independent of arsenite concentration.

Table II. Effect of Hydroxide Ion in the Reaction between $Fe(CN)_6^{3-}$ and As^{III} [a]

[NaOH], M	k_0, M^{-1} s^{-1}, for $[As^{III}]$, M: 8.0×10^{-3} (45 °C)	2.0×10^{-3} (45 °C)	4.0×10^{-3} (45 °C)	2.0×10^{-3} (35 °C)	2.0×10^{-3} (55 °C)
0.0010	0.017				
0.0020	0.083	0.017	0.0060		
0.0030	0.15				
0.0040	0.205	0.083	0.14		
0.0060	0.24	0.17			
0.0080	0.26				
0.010	0.30	0.28	0.26	0.22	0.38
0.018			0.37		
0.020	0.395	0.41		0.34	0.53
0.022			0.40		
0.026			0.47		
0.030	0.52	0.52	0.52	0.43	0.73
0.040	0.59	0.67	0.74	0.56	0.89
0.050	0.83	0.77		0.68	1.0
0.060		0.94	0.96	0.78	1.2
0.070	1.10	1.1		0.91	1.45
0.080		1.25		1.02	1.55
0.090	1.25	1.4		1.15	1.7
0.100	1.4	1.5	1.3	1.25	1.9
0.120	1.7	1.8	1.7		
0.140	1.9	2.0	1.9	1.70	2.55
0.160	2.3	2.3	2.2		
0.180		2.6	2.2		
0.200	2.7	2.8	2.7	2.4	3.6
0.220		3.1	2.9		
0.250		3.5	3.6		
0.300	4.0	4.2	4.2	3.5	5.3
0.400	5.3	5.3	5.6	4.6	6.75
0.500	6.6	6.7	6.7	5.6	
0.600	8.0				
0.700	9.4				

[a] $[Fe(CN)_6^{3-}] = 8 \times 10^{-4}$ M; $I = 2.0$ M (adjusted with NaCl).

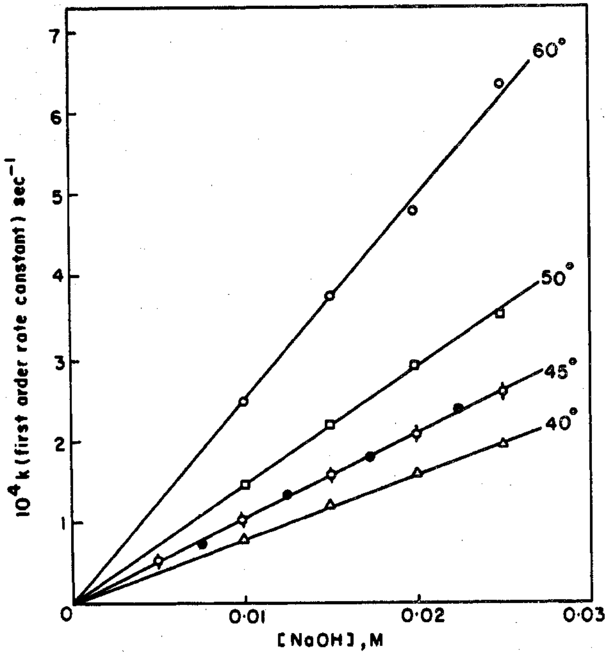

Figure 1. Variation of [NaOH] in the reaction between $Fe(CN)_6^{3-}$ and As^{III} at different temperatures when $[OH^-]/[As^{III}] < 0.5$; $[Fe(CN)_6^{3-}] = 8 \times 10^{-4}$ M; $I = 2.0$ M; 415 nm; $[As^{III}] = 8 \times 10^{-2}$ M except for closed circles (●), where $[As^{III}] = 0.12$ M.

Hydroxide Ion Dependence. Dependence on hydroxide ion was studied by varying the concentration of sodium hydroxide from 1×10^{-3} to 5×10^{-1} M at three different concentrations of arsenite. The results are given in Table II. There is no

Table III. Rate Constants and Activation Parameters for the Reaction between $Fe(CN)_6^{3-}$ and As^{III} [a]

Rate const	35 °C	45 °C	55 °C	E_a, kcal mol^{-1}	S, cal mol^{-1} deg^{-1}
10^3k_1, M^{-1} s^{-1}	7.8 ± 0.4 (at 40 °C)	10 ± 0.9	14 ± 0.7 (at 50 °C)	11.8 ± 0.5	−32 ± 2
k_2, M^{-2} s^{-1}	0.25 ± 0.025	0.35 ± 0.025	0.45 ± 0.05	6.4 ± 0.7	−43 ± 3
k_3K_3, M^{-3} s^{-1}	11 ± 0.1	13 ± 0.2	16 ± 0.4	3.75 ± 1.46	−42 ± 3

[a] $I = 2.0$ M (adjusted with NaCl).

clear-cut first-order dependence on the hydroxide ion concentration. Variation of hydroxide ion concentration was also investigated when As^{III} was large. Figure 1 shows this variation at four different temperatures, 40, 45, 50, and 60 °C. The rate thus has a first-order dependence on $[OH^-]_T$ when As^{III} is large. From the slopes of these lines k_1 (defined later) at different temperatures has been calculated.

Ferrocyanide Dependence. The concentration of hexacyanoferrate(II) was varied in the range $(1–5) \times 10^{-3}$ M in the presence of 2.0 M sodium perchlorate to maintain almost constant ionic strength. No effect of hexacyanoferrate(II) was observed. The conclusion of Krishna and Singh[1] that it has effect on the rate may be erroneous owing to the variation in the ionic strength.

Energy and Entropy of Activation. The reaction was studied at 35, 45, and 55 °C with respect to the hydrogen ion dependence to determine the activation parameters for the different reaction paths, E_a and $\Delta S^{\ddagger}$, which are given in Table III.

Discussion

From a Raman spectral study Loehr and Plane[11] have reported that in hydroxide solutions mainly $As(OH)_3$, $AsO(OH)_2^-$, $AsO_2(OH)^{2-}$, and AsO_3^{3-} are present. Similar views have been expressed by others[12,13] too. It is reported[14] that addition of OH^- to $As(OH)_3$ converts three-coordinated As^{III} to four-coordinated $As(OH)_4^-$ rather than abstracting H^+ from H_3AsO_3 to form $H_2AsO_3^-$. The species $As(OH)_4^-$ and $H_2AsO_3^-$ differ only in the degree of hydration and it would be difficult to predict the precise form of As^{III} in such solutions. Equilibria 1–3 have been suggested[2,15] in alkaline

$$H_3AsO_3 + OH^- \overset{K_1}{\rightleftharpoons} H_2AsO_3^- + H_2O \tag{1}$$

$$H_2AsO_3^- + OH^- \overset{K_2}{\rightleftharpoons} HAsO_3^{2-} + H_2O \tag{2}$$

$$HAsO_3^{2-} + OH^- \overset{K_3}{\rightleftharpoons} AsO_3^{3-} + H_2O \tag{3}$$

solutions of H_3AsO_3. Hexacyanoferrate(III) reacts with all of the species and hydroxide ion dependence shows that the order of reactivity of these species is $AsO_3^{3-} > HAsO_3^{2-} > H_2AsO_3^-$ and that H_3AsO_3 is either not reactive at all or much less reactive than $H_2AsO_3^-$. The complete rate law is

$$-d[Fe(CN)_6^{3-}]/dt = [Fe(CN)_6^{3-}](k_1[H_2AsO_3^-] + k_2[HAsO_3^{2-}] + k_3[AsO_3^{3-}]) \tag{4}$$

$$-d[Fe(CN)_6^{3-}]/dt = \frac{[Fe(CN)_6^{3-}][As^{III}]_T(k_1K_1[OH^-] + k_2K_1K_2[OH^-]^2 + k_3K_1K_2K_3[OH^-]^3)}{1 + K_1[OH^-] + K_1K_2[OH^-]^2 + K_1K_2K_3[OH^-]^3} \tag{5}$$

where $[Fe(CN)_6^{3-}]$ and $[As^{III}]_T$ are the total concentrations of the species concerned and $[OH^-]$ is the equilibrium concentration. Under the condition of constant $[OH^-]_T >> [As^{III}]_T$ and $[Fe(CN)_6^{3-}]$, the rate law is

$$-d[Fe(CN)_6^{3-}]/dt = k_0[Fe(CN)_6^{3-}][As^{III}]_T \tag{6}$$

and under the condition $[As^{III}]_T >> [Fe(CN)_6^{3-}]$ and $[OH^-]_T$, the rate law becomes

$$-d[Fe(CN)_6^{3-}]/dt = k[Fe(CN)_6^{3-}] \tag{7}$$

Association constants K_1 and K_2 were calculated from the acid dissociation constants[16-19] of arsenious acid using the equations given by Antikainen and co-workers,[16,17] the ionic product of water given by Hugel,[20] and $\Delta H = -13.62$.[21] K_1 was found to be 4.88×10^6, 3.54×10^6, 2.68×10^6, and 2.12×10^6, and K_2 was found to be 210, 190, 170, and 155 at $I = 2.0$ M and 25, 35, 45, and 55 °C, respectively. The third dissociation constant of arsenious acid and the association constant K_3 are not known. However, by comparing the third dissociation constants of H_3AsO_4 and H_3PO_4, K_3 of equilibrium 3 could be estimated to be less than 1×10^{-2}. In the variation of hydroxyl ion concentration, the rate does not tend to have a limiting value even at ratios of $[OH^-]_T/[As^{III}]_T \simeq 1000$. Thus K_3 must be small. When $[OH^-]_T/[As^{III}]_T$ is less than 1 and since K_1 is large, the predominant As^{III} species would be $H_2AsO_3^-$. Since $[OH^-]$ is in deficiency, the concentration of $H_2AsO_3^-$ would be determined by $[OH^-]_T$ alone. In this case expression 4 reduces to (8). A plot of k vs. $[OH^-]_T$ made in

$$-d[Fe(CN)_6^{3-}]/dt = k_1[Fe(CN)_6^{3-}][H_2AsO_3^-] = k_1[Fe(CN)_6^{3-}][OH^-]_T \tag{8}$$

Figure 1 shows straight lines passing through the origin in conformity with relation 8. Thus k_1 values could be calculated.

When $[OH^-]_T > [As^{III}]_T$ and since K_1 is large and K_3 is small, the rate law (5) reduces to (9). By rearrangements

$$-d[Fe(CN)_6^{3-}]/dt = \frac{[Fe(CN)_6^{3-}][As^{III}]_T(k_1 + k_2K_2[OH^-] + k_3K_2K_3[OH^-]^2)}{1 + K_2[OH^-]} \tag{9}$$

we obtain (10).

$$\frac{k_0(1 + K_2[OH^-]) - k_1}{K_2[OH^-]} = k_2 + k_3K_3[OH^-] \tag{10}$$

Concentration of free OH^- was calculated by successive approximations from the equilibrium and mass balance relations.[22,23] Now since k_1 is known, a plot of the left-hand side of expression 10 against free $[OH^-]$ would yield a straight line with nonzero intercept as shown in Figure 2. k_2 and k_3K_3 were estimated from the intercept and slope of the line and these values along with k_1 are given in Table III.

The maxima in the curves mentioned under arsenite dependence are typical of such complicated systems and are similar to those obtained in the chloride ion catalyzed oxidation[24] of H_3PO_3 by Tl^{III}. This will always happen if a number of species in the system are reactive so that the rate depends on the ratio of the two reactant concentrations. No particular significance could be attached to the maximum except that it occurs at $[OH^-]_T/[As^{III}] \simeq 4.0$.

The spectrophotometric results also indicate that at least two species of As^{III} exist in hydroxide solutions and that the formation constant must be large. Mixtures of As^{III} and OH^- show a peak in the region 190–200 nm and obey Beer's law at the peak wavelength, for the same ratio of $[OH^-]_T/[As^{III}]$, suggesting a large value for K_1. Another characteristic of these results is the shift of the peak of the mixtures with the increase in the ratio $[OH^-]_T/[As^{III}]$ or with the larger but equal

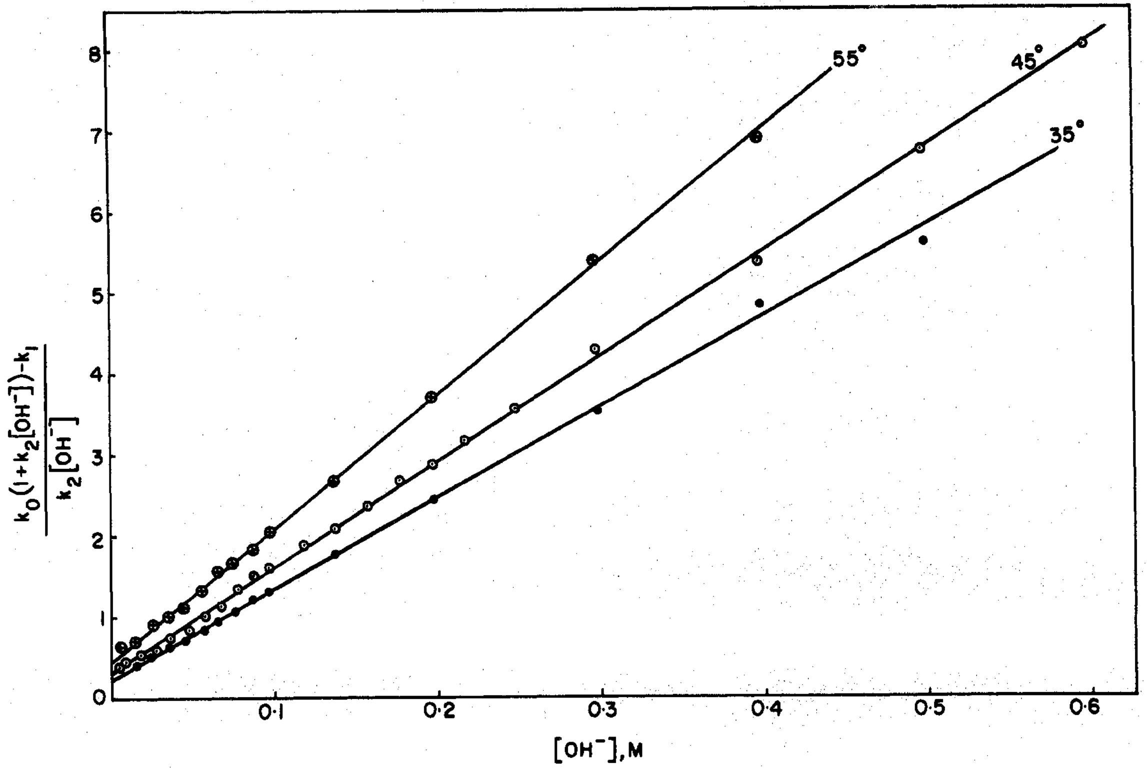

Figure 2. Hydroxide ion dependence in the reaction between $Fe(CN)_6^{3-}$ and As^{III}; $[Fe(CN)_6^{3-}] = 8.0 \times 10^{-4}$ M; $[As^{III}] = 2.0 \times 10^{-3}$ M; $I = 2.0$ M (adjusted with NaCl).

concentrations of $[OH^-]_T$ and $[As^{III}]$. This suggests that at least two species are being formed from H_3AsO_3 in the system.

The entropy of activation for different reactions is negative. Since the reactants are similarly charged, the activated complex would be more charged and would be accompanied by the decrease of entropy.[25] The magnitudes of the entropy of activation suggest ion pairing of Na^+ and $Fe(CN)_6^{3-}$. The positive salt effect found by earlier workers[1,2] is in conformity with the reaction occurring between similarly charged ions and further the magnitude of the salt effect also suggests ion pairing between Na^+ and $Fe(CN)_6^{3-}$ and/or Na^+ and arsenite species. A discussion on salt effect has already been given in an earlier paper.[26]

It has already been mentioned in the Introduction that the previous workers[1,2] who studied this reaction failed to obtain a clear-cut hydrogen ion dependence in a wide range of its concentration. A comparison of the results, therefore, is difficult, particularly because the ionic strengths are not the same. If we regard the order with respect to hydrogen ion to be 1, the value of $k_0/[OH^-]$ at $[H^+] > 0.1$ M is found to be ~ 13 M^{-2} s^{-1} at $I = 2.0$ M and at 45 °C. The corresponding value obtained by Mushran and co-workers[2] is 4.13 M^{-2} s^{-1} and that obtained by Krishna and Singh[1] is 2.8 M^{-2} s^{-1} at 40 °C and $I = 0.2$ M. In view of the large positive effect of ionic strength on the rate, our value of 13 M^{-2} s^{-1} seems to be in order.

A general comparison of the rate and activation parameters with those of other $Fe(CN)_6^{3-}$ reactions is also difficult because of the different $[OH^-]$ dependences and conditions. However, a comparison with the oxidation of antimony(III)[27] and hypophosphite[26] shows that the oxidation of Sb^{III} has about the same rate while oxidation of H_3PO_2 is slower than that of As^{III}. The second-order rate constant for Sb^{III} oxidation is 1.74 M^{-1} s^{-1} at 35 °C and 1.0 M NaOH ($I = 1.0$ M) and that for H_3PO_2 is 0.105 M^{-1} s^{-1} at 35 °C and 4.0 M NaOH ($I = 4.7$ M). The extrapolated value of k_0 for the oxidation of As^{III} at 1.0 M NaOH is about 13 M^{-1} s^{-1} at 45 °C and $I = 2.0$ M.

Registry No. $Fe(CN)_6^{3-}$, 13408-62-3; H_3AsO_3, 13464-58-9; OH^-, 14280-30-9.

References and Notes

(1) B. Krishna and H. S. Singh, *J. Inorg. Nucl. Chem.*, **31**, 2964 (1969).
(2) M. C. Agarwal, V. K. Jindal, and S. P. Mushran, *J. Inorg. Nucl. Chem.*, **32**, 1257 (1970).
(3) I. M. Kolthoff, E. J. Meehan, M. S. Tsao, and Q. W. Choi, *J. Phys. Chem.*, **66**, 1233 (1962).
(4) A. W. Adamson, *J. Phys. Chem.*, **56**, 859 (1952).
(5) C. W. Davies, "Ion Association", Butterworths, London, 1962, Chapter 13.
(6) C. W. Davies, *Prog. React. Kinet.*, Chapter 6 (1963).
(7) J. H. Swinehart, *J. Inorg. Nucl. Chem.*, **27**, 2313 (1967).
(8) V. K. Jindal, M. C. Agarwal, and S. P. Mushran, *J. Chem. Soc. A*, 622 (1971).
(9) U. S. Mehrotra, M. C. Agarwal, and S. P. Mushran, *J. Phys. Chem.*, **73**, 1996 (1969).
(10) M. Latshaw, *J. Am. Chem. Soc.*, **47**, 793 (1925).
(11) T. M. Loehr and R. A. Plane, *Inorg. Chem.*, **7**, 1708 (1968).
(12) G. Jander and H. Holfman, *Z. Anorg. Allg. Chem.*, **296**, 134 (1958).
(13) C. S. Bhatnagar and H. Govind, *Z. Naturforsch., B*, **21**, 190 (1966).
(14) A. Simon and R. Pactzold, *Z. Anorg. Allg. Chem.*, **301**, 246 (1959).
(15) V. N. Kochegarov and T. P. Lomakina, *Elektrokhimiya*, **2**, 240 (1966); D. Y. Evdokimov, *Med. Promst. SSSR*, **11** (4), 39 (1957).
(16) P. J. Antikainen and K. Tevenen, *Suom. Kemistil. B*, **34**, 3 (1961).
(17) P. J. Antikainen and V. M. K. Rossi, *Suom. Kemistil. B*, **32**, 185 (1959).
(18) P. Goldfinger, *Z. Phys. Chem., Abt. B*, **19**, 219 (1932).
(19) P. Souchay, *Bull. Soc. Chim. Fr.* **13**, 160 (1946).
(20) R. Hugel, *Bull. Soc. Chim. Fr.* **32**, 968 (1965).
(21) R. N. Goldberg and L. G. Heplar, *J. Phys. Chem.*, **72**, 4654 (1968).
(22) G. M. Waind, *Discuss. Faraday Soc.*, **29**, 136 (1960).
(23) J. N. Butler, "Ionic Equilibrium", Addison-Wesley, Reading, Mass., 1964, p 82.
(24) K. S. Gupta, Ph.D. Thesis, Rajasthan University, 1970.
(25) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", Wiley, New York, N.Y., 1960, p 145.
(26) D. Mohan, V. K. Chhabra, and Y. K. Gupta, *J. Chem. Soc., Dalton Trans.*, 1737 (1975).
(27) D. Mohan and Y. K. Gupta, unpublished work.